

THE ELECTRONIC STRUCTURE OF SULFUR, SELENIUM AND TELLURIUM DONORS IN SILICON

BY
ERIK JANZÉN

I																VIII											
1 H	II'															III IV V VI VII										2 He	
3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne						
11 Na	12 Mg	III'														13 Al	14 Si	15 P	16 S	17 Cl	18 Ar						
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr										
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe										
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn										
87 Fr	88 Ra																										
		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu												



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37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe								
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87	Fr	88	Ra																																								
																58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu

THE ELECTRONIC STRUCTURE
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BONDORS IN SILICON
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The electronic structure of sulfur, selenium and tellurium donors in silicon.
by

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This thesis is a study of how the chalcogens S, Se and Te behave as dopants in silicon. The work is presented in six papers.

- I Deep sulfur-related centers in silicon
(Journal of Applied Physics 51, 4212 (1980))
- II Electronic properties of selenium-doped silicon.
(Journal of Applied Physics 51, 3740 (1980))
- III Chemical identification of deep energy levels in Si:Se.
(Journal of Applied Physics 51, 6238 (1980))
- IV Capture, emission and recombination at a deep level via an excited state.
(Journal of Physics C: Solid State Physics 13, 6157 (1980))
- V Tellurium donors in silicon.
(Physical Review B, in press)
- VI Multivalley splitting of 1s states for sulfur, selenium and tellurium donors in silicon.
(manuscript)

Co-authors are H.G. Grimmeiss (I-VI), B. Skarstam (I-IV), A. Lodding (III), G.J. Rees (IV), H. Ennen (V), O. Schirmer (V), J. Schneider (V), R. Wörner (V), C. Holm (V), E. Sirtl (V), P. Wagner (V) and K. Larsson (VI).

Chalcogens in silicon are interesting for several reasons, for instance their applications in infrared detectors ¹⁻⁶). Extrinsic-silicon infrared detectors for wavelengths corresponding to the atmospheric transmission windows (3-5, 8-14 μm) are of great importance because of their possible use with charge-coupled devices in monolithic thermal imaging systems. The limiting detectivity of an infrared detector is controlled

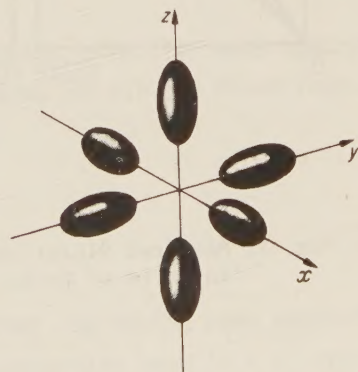
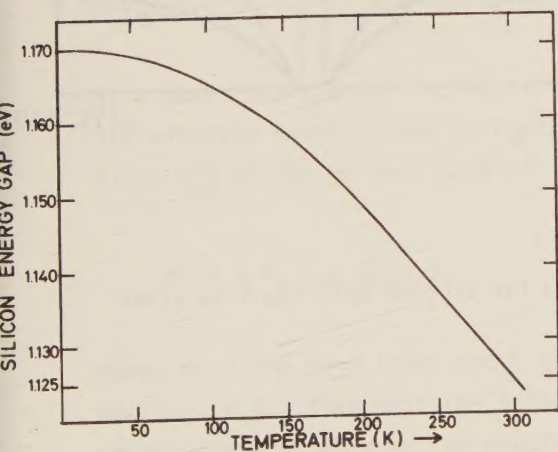
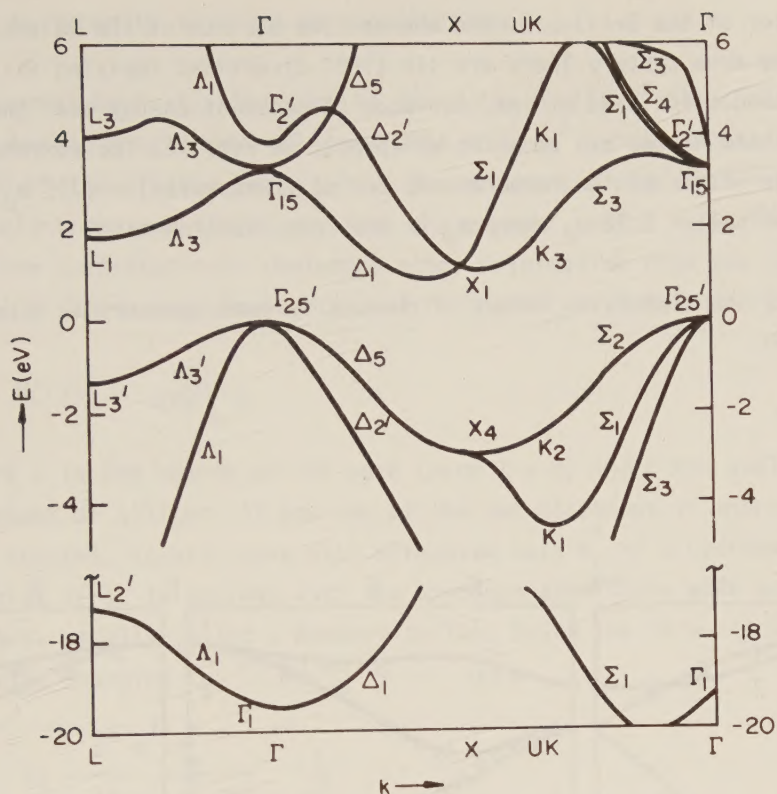
by the noise due to the generation and recombination of charge carriers as influenced by the background radiation. To reach this limit, it is necessary that the temperature be sufficiently low. The thermally generated charge carriers must then be much fewer than those generated by the background radiation. Hence, the level giving rise to the photoresponse should be as deep as possible. At present In (0.16 eV) is used for this purpose in the 3-5 μm range but the drawback is the low temperature needed, 60 K. It would be much more convenient if liquid nitrogen at normal pressure could be used as coolant. A dopant with slightly deeper energy levels is therefore required. Chalcogens in silicon have several levels between 0.2 and 0.3 eV. This is one reason for the growing interest in these dopants. The possibility of growing epitaxial layers using vapour transport with chalcogens as carrier is important in this context. The technique is described in paper V and in Ref. 7. Chalcogens in silicon are also interesting from a more fundamental viewpoint because of their possible behaviour as double donors in analogy with the helium atom. Double donors have been treated theoretically in several works⁸⁻¹¹). Experimentally the main interest has hitherto been focused only on sulfur (see references in paper I).

The remainder of this introduction will be devoted to a discussion of a few subjects important for the thesis. First, some properties of the host material silicon are treated. Second, the energy spectrum expected when chalcogens are introduced into silicon is discussed. Third, the dynamical behaviour of the impurity-host system, i.e. how electrons are captured to and emitted from the impurity level is outlined. Fourth, a survey of the experimental techniques used in this thesis will be given. Finally, the papers will be summarized and their results compared with other results in the literature.

Silicon

Silicon belongs to group IV of the periodic table. It crystallizes in a diamond structure with lattice constant $a = 5.43 \text{ \AA}$. The electrons in the outer shell form four sp^3 hybrid orbitals, directed tetrahedrally towards the nearest neighbours 2.32 $\text{\AA}$ apart.

The bandstructure of silicon is shown in Fig. 1a. The bandgap is indirect and its temperature dependence is given in Fig. 1b. The minimum of the conduction band is in the [100] direction $0.85 \cdot \frac{2\pi}{a}$ away from



the center of the Brillouin zone whereas the maximum of the valence band is at the zone center. There are six [100] directions implying six equivalent conduction band minima. Surfaces of constant energy near the conduction band minima are shown as ellipsoids in Fig. 1c. The corresponding effective masses at low temperatures are m_t (transverse) = $0.19 m_0$ and m_l (longitudinal) = $0.92 m_0$ where m_0 is the free-electron mass.

In Fig. 2 the dispersion curves of phonons in some symmetrical directions are shown.

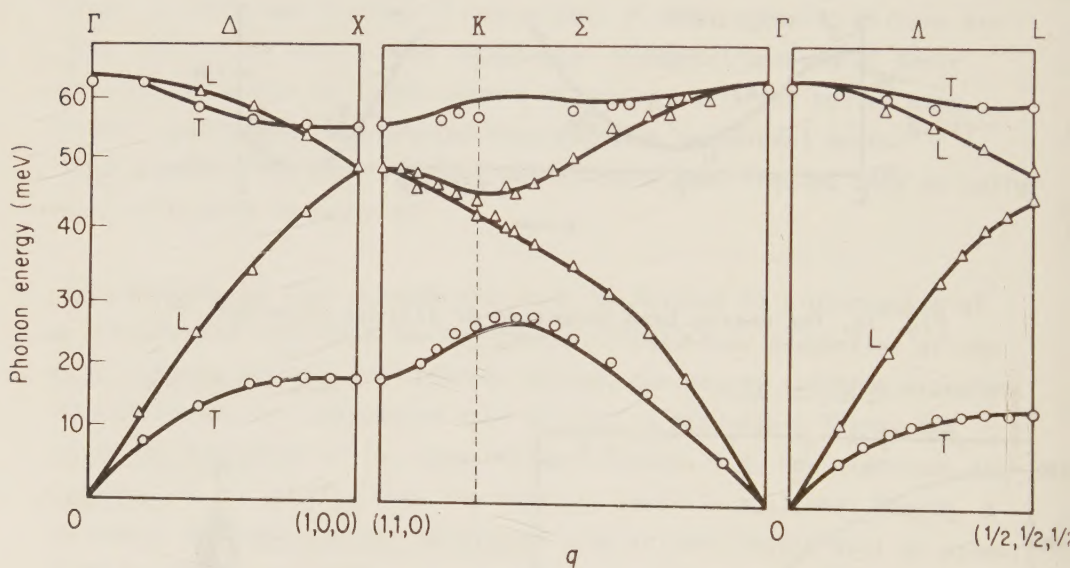


Fig. 2. Measured vibrational spectrum for Si from Ref. 13. $\bar{q}$ is given in units of $2\pi/a$.

Energy spectrum

The energy spectrum of chalcogen centers in silicon is closely related to their physical location in the lattice. If the chalcogen atom simply replaces a silicon atom, a descriptive model can easily be constructed [14-17]

Such an impurity is known as substitutional.

Chalcogens have six electrons in the outer shell. If the chalcogen atom is substitutional, four of these will form sp^3 hybrid orbitals to match those of the silicon host. Let us for a moment assume that the remaining two electrons are taken away from the crystal, which is perfect except for one substitutional chalcogen atom. Originating from the chalcogen core, a screened Coulomb potential $U(r)$ will exist in the crystal.

$$U(r) = - \frac{Ze}{4\pi\epsilon\epsilon_0 r} \quad (1)$$

where Z is the charge of the core (here $Z = 2$) and ϵ the dielectric constant of silicon. If now one of the two electrons is introduced into the crystal, it will move with effective mass m_e^* in a hydrogen-like potential $U(r)$. In analogy with the hydrogen atom there will be bound states, usually called a Rydberg series, below the conduction band, with binding energies E_B

$$E_B = \frac{Z^2 e^4 m_e^*}{(4\pi\epsilon\epsilon_0)^2 2\hbar^2} \frac{1}{n^2} \quad (2)$$

where $n = 1, 2, \dots$. If the first electron is in its lowest bound state, it will partly screen the core charge. Introduction of the second electron into the crystal can then, at least for the excited states, be described in a similar way (but with $Z = 1$).

In a more rigorous derivation of this "hydrogenic effective mass theory", the electron wavefunction ψ is expanded in terms of all the Bloch functions $\psi_{n\vec{k}}^0$ of the perfect crystal.

$$\psi(\vec{r}) = \sum_{n\vec{k}} F_{n\vec{k}} \psi_{n\vec{k}}^0(\vec{r}) \quad (3)$$

Here, n is the band index and $\vec{k}$ the wave vector. By making some approximations, e.g., that only the bottom of the conduction band ($n = 0$) contributes appreciably to the wavefunction ψ , the original eigenvalue problem for the imperfect crystal $H\psi = E_r\psi$ is reduced to the following equation

$$\left[-\frac{\hbar^2}{2m_e^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(r) \right] F(\vec{r}) = E_B F(\vec{r}) \quad (4)$$

which is similar to the Schrödinger equation for the hydrogen atom if modification due to the dielectric screening, the charge and the effective mass are made. $F(\vec{r})$ is the inverse fouriertransform of $F_{0\vec{k}}$. Thus the energy solutions of the Rydberg series are given by (2) and the corresponding $F(\vec{r})$ are modified hydrogenic wavefunctions. The complete wavefunction $\psi(\vec{r})$ is then given by

$$\psi(\vec{r}) = F(\vec{r}) \psi_{k_0}^0(\vec{r}) \quad (5)$$

where $\psi_{k_0}^0(\vec{r})$ is the Bloch function close to the bottom of the conduction band. $F(\vec{r})$ differs for every state in the Rydberg series whereas $\psi_{k_0}^0$ is the same. The different states are, as usual, labelled 1s, 2s, 2p etc. (see Fig. 3a). Eq. 5 may be interpreted in terms of a slow modulation of the Bloch state $\psi_{k_0}^0$ by the function $F(\vec{r})$ as a result of the weak Coulomb attraction of the donor ion.

A problem arises when Eq. 2 is used for calculating energy positions. What value of m_e^* should be used? As pointed out in the previous section, the effective mass at the bottom of the conduction band in silicon is anisotropic. In fact, Eq. 4 is only valid if the effective mass is isotropic and hence it has to be modified for silicon. If the j th minimum of the conduction band lies along the z-axis the equation will be

$$\left[-\frac{\hbar^2}{2m_t^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{\hbar^2}{2m_\lambda^*} \frac{\partial^2}{\partial z^2} + U(r) \right] F_j(\vec{r}) = E F_j(\vec{r}) \quad (6)$$

The symmetry of the Hamiltonian is now no longer spherical but cylindrical. The non-spherical part of the Hamiltonian will mix states with the same parity (ℓ odd or even) and the same projection (m) of angular momentum (ℓ) along the z-axis. The result is that the accidental degeneracy of states with the same n but different ℓ no longer holds and that states with the same ℓ but with different values of $|m|$ will split up (see Fig. 3b). For convenience, the hydrogenic notation is still used although each level now represents a mixture of all hydrogenic states with the appropriate parity and projection of angular momentum. The notation only indicates the hydrogenic state into which each level would reduce in the limit $\frac{m_t^*}{m_\lambda^*} \rightarrow 1$.

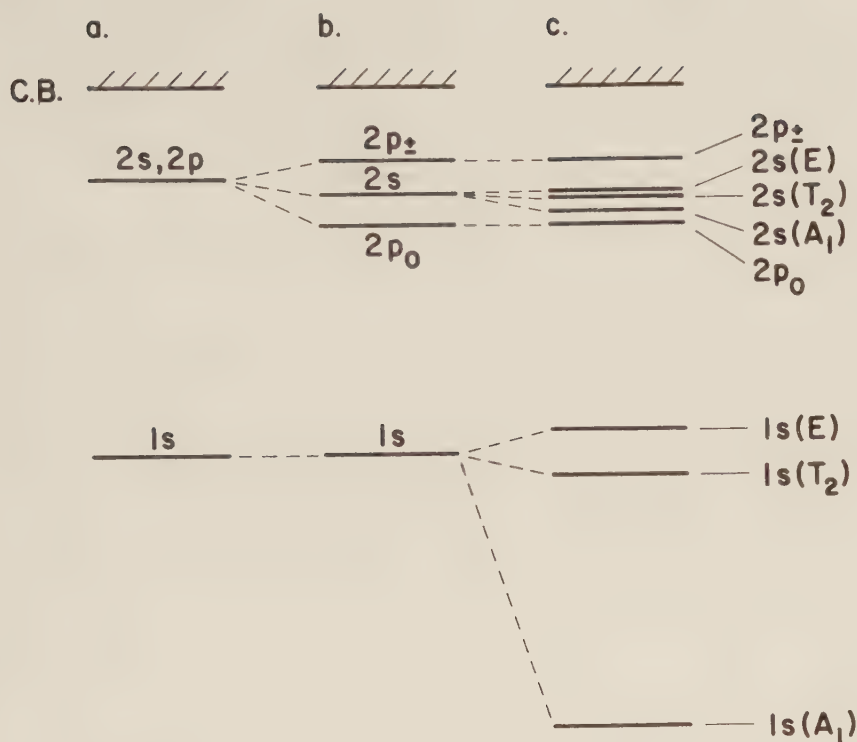


Fig. 3. The lowest energy states of an electron bound to a donor in a Coulomb potential.

- If the effective mass is isotropic (e.g., GaAs), the ns and np states will be degenerate.
- If the effective mass is anisotropic (e.g., Si), this degeneracy will break.
- In addition the $1s$ and $2s$ states will split due to multi-valley interactions in silicon.

Energy level calculations of this kind with $Z=1$ have been carried out by Faulkner¹⁷⁾. Agreement with experimental results from group V donors in silicon is extremely good except for the 1s and 2s states. To extend Faulkner's calculation to $Z=2$ is not difficult. The energy level will simply be four times deeper. Hence, it is to be expected that his calculation will also be valid for the excited states (except 2s) of chalcogens in silicon and for both $Z=1$ and $Z=2$.

There are two main reasons why the effective mass theory described above fails to predict the correct energy positions of the 1s and 2s states. First, an electron in an s-state, especially if it is 1s, will spend an appreciable amount of time close to the donor ion, a region which is sometimes referred to as the central cell. In this region, the attractive potential is stronger than the screened Coulomb potential outside, which makes the energy level deeper. Second, since there are six equivalent conduction band minima in silicon, the electron wavefunction of every state should be written as a linear combination of wavefunctions belonging to the different minima¹⁵⁾ (cf. Eq. 5)

$$\psi(\vec{r}) = \sum_{j=1}^6 \alpha_j F_j(\vec{r}) \psi_{\vec{k}_j}^0(\vec{r}) \quad (7)$$

Here, $F_j(\vec{r})$ is the hydrogen-like envelope function belonging to the j th minimum and $\psi_{\vec{k}_j}^0(\vec{r})$ the corresponding Bloch function of the perfect crystal. This makes every s, p_0 , $p_{\pm}$ state six-, six-, and twelve-fold degenerate, respectively, excluding spin. If, however, the potential acting upon the electron is strong, $F_j(\vec{r})$ will be localized close to the donor ion. While still mainly centered around the j th minimum, $F_j(\vec{r})$, the fouriertransform of $F_j(\vec{r})$, will then be spread out into the Brillouin zone. If the $F_j(\vec{k})$ from two different minima (valleys) overlap, the approximations that led to Eq. 6 are no longer valid. New terms called intervalley terms will appear in the Hamiltonian^{9,10,18,19)}. Only s-states have non-negligible intervalley terms, since the p, d,... states all have vanishing amplitudes in the central cell region where the potential is strongest. These latter states are well described by the "one-valley" effective mass theory (Eq. 6).

If the chalcogen atom occupies a substitutional site, its surroundings are tetrahedral. The central cell potential will therefore split each six-fold degenerate s-state into a singlet (A_1), a triplet (T_2) and a doublet (E) (see Fig. 3c). The splitting is, of course, largest for 1s. Sometimes it is referred to as valley-orbit splitting. The ground state should be 1s(A_1)

since, in contrast to $1s(A_1)$, $1s(T_2)$ and $1s(E)$ have a node at the chalcogen atom and are therefore less affected by the central cell potential¹⁵⁾. For the neutral chalcogen centers ($Z=1$) one may expect that, due to insufficient screening, the effective charge seen by the outer electron is larger than one. However, in papers V and VI it is shown experimentally that this effect is considerable only for the ground state $1s(A_1)$ for which the two electrons are equivalent. An additional splitting of the $1s(T_2)$ state due to spin-orbit effects may occur (see Ref. 20-22 and paper IV). Valley-orbit split $1s$ -states have earlier been observed for group V donors in silicon²⁰⁾.

It is not obvious that the foreign chalcogen atom should occupy a substitutional site when introduced into the silicon lattice. One cannot exclude the possibility of any interstitial site or the formation of complexes such as chalcogen pairs, chalcogen-vacancy or chalcogen with any other impurities present in the crystal. The construction of models for the energy spectrum in these cases is not immediately obvious.

Dynamical behaviour

When an electron goes from the conduction band to a localized state in the bandgap, the energy must be released in some form. This recombination energy may be in the form of photons, phonons or kinetic energy of free particles. The relative importance of the various processes depends on such factors as temperature, the amount of energy that has to be carried away, etc.

In the previous section it was shown that both neutral and singly ionized substitutional chalcogen impurities have excited states close to the conduction band, which makes it probable that the recombination energy is partly carried away in the form of a cascade of phonons. The electron is first captured in a highly-excited state. It then diffuses down the ladder of excited states emitting one or very few phonons at every step. The probability for re-emission back to the conduction band decreases with increasing binding energy. Since excited states are less closely spaced further down the ladder, the electron will finally reach a state where the next step will require a multiphonon transition or the emission of a photon, both of which are slow processes. If the temperature is low enough, re-emission from this state will be negligible. Hence, the electron capture cross section, as measured by the rate at which electrons leave the conduction band, is not affected by the subsequent transitions.

The cascade capture model was first proposed by M. Lax ²³⁾ and could successfully explain the enormous capture cross sections observed for shallow donors in silicon and germanium. The calculated temperature dependence varies from T^{-4} to T^{-1} depending both on temperature and on the phonons involved.

In a recent paper, Abakumov ²⁴⁾ claims that the probability for re-emission from highly excited states is smaller than shown by Lax's calculations. Hence Abakumov's capture cross sections is larger than Lax's and the temperature dependence is T^{-3} or T^{-1} depending on whether acoustical or optical phonons are involved.

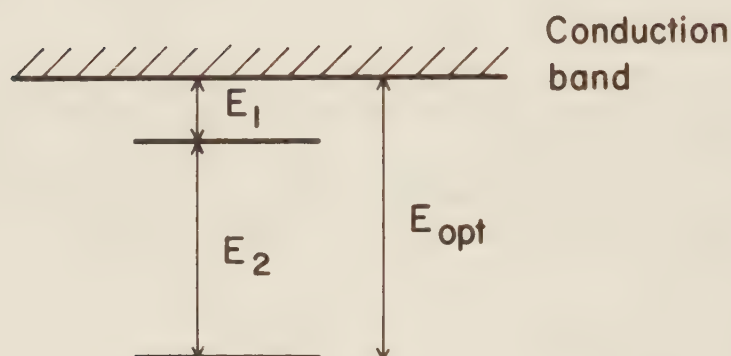


Fig. 4. Energy level scheme of a center whose dynamical behaviour can be described in terms of two-stage capture and emission processes. E_1 is the energy distance between the lowest cascade state and the conduction band, E_2 the energy separation between the ground state and the lowest cascade state and E_{opt} the ground state binding energy as obtained from absorption measurements.

At high temperatures the situation is quite different. The electron will still diffuse down to the lowest state, E_1 below the conduction band, accessible by a phonon cascade (see Fig. 4). The subsequent, slow transition will now have to compete with thermal re-emission back to the conduction band, which of course decreases the capture rate. In Ref. 25 and paper IV, it is shown that in the high temperature limit the electron capture cross section σ_n^t is given by the expression

$$\sigma_n^t = \frac{v_2 \cdot g_x}{V_{th} N_c} e^{E_1/kT} \quad (8)$$

where v_2 is the rate of the slow transition mentioned above and g_x the degeneracy of the lowest "cascade" state.

It is not immediately obvious to what energy state E_1 should correspond. If all kinds of phonons are involved, the lowest "cascade" state for neutral donors would be $1s(T_2)$ and for ionized donors $2p_0$ or perhaps $2s(A_1)$. The energy position of $2s(A_1)$ is unknown for all chalcogen centers but in view of the large multivalley splitting for $1s$ -states, it is not unreasonable to believe that $2s(A_1)$ is below $2p_0$. In actual fact, recent calculations by Altarelli²⁶⁾ show that the $2s(A_1)$ and $2p_0$ states of ionized donors should lie 73 and 46 meV respectively below the conduction band. On the other hand, if only low energy acoustical phonons are involved, the lowest "cascade" state will be $2p_0$ or $2s(A_1)$ for neutral donors. The situation is more complex for singly-ionized donors since the excited states are less closely spaced than for neutral donors. Depending on the energy positions of the multivalley split $2s$ -states, the lowest "cascade" state may vary from $2s(A_1)$ to $2p_{\pm}$.

The emission of electrons from the ground states will also go via excited states. In Ref. 25 and paper IV, emission is treated as a two-stage process. At high temperatures, the transition (energy E_2) from the ground state to the lowest cascade state is the rate-limiting process and the emission is given by the expression (see Fig. 4)

$$e_n^t = \frac{g_x}{g_g} v_e^{-E_2/kT} \quad (9)$$

where g_g is the degeneracy of the ground state. For low temperatures, we get instead

$$e_n^t \sim e^{-(E_1+E_2)/kT} \quad (10)$$

The relation between the thermal emission rate and the capture cross section is given by the detailed balance relationship

$$e_n^t = \sigma_n^t v_{th} N_c e^{-\Delta G_n^t/kT} \quad (11)$$

ΔG_n^t is the change in Gibb's free energy when an electron is emitted into the band. The formalism is discussed further in papers I and II ^{27,28}).

An electron can also be transferred to an excited state or directly into the conduction band by absorbing a photon. If the temperature is high enough, there is a possibility for combined photon/phonon-assisted electron emission, i.e., first optical transfer to an excited state and then thermal emission into the conduction band (photothermal ionization) ²⁹). By varying the photon energy, the spectral dependence of the photoionization cross section can be obtained, monitored by photoconductivity, photocapacitance, absorption, etc.

Electric dipole optical transitions from the ground state to excited states are governed by selection rules. For instance, the initial and final states must have different parities, i.e., transitions $s \rightarrow p, f, h$ etc., are allowed whereas transitions $s \rightarrow s, d$ etc., are forbidden. Transitions among multivalley split s-states are obviously parity-forbidden. They have therefore not been observed for the shallow donors P, As and Sb, since even the ground states of these donors are nearly effective mass like. To be able to see transitions between s-states, at least one of the states has to be mixed with a state of different parity (p, f etc.). The same effect would be obtained if at least one of the states consisted partly of wavefunctions from other bands. Transitions $1s(A_1) \rightarrow 1s(T_2)$ have been observed for Bi and for all chalcogen centers, but not $1s(A_1) \rightarrow 1s(E)$. The reason is that $1s(A_1) \rightarrow 1s(T_2)$ is symmetry-allowed whereas $1s(A_1) \rightarrow 1s(E)$ is symmetry forbidden. In the same way, $1s(A_1) \rightarrow 2s(T_2)$ may be seen but not $1s(A_1) \rightarrow 2s(A_1)$ or $1s(A_1) \rightarrow 2s(E)$.

Experimental techniques

In this study of the chalcogens in silicon four completely different experimental techniques have been used: Junction space charge techniques, optical absorption, electron spin resonance (ESR) and secondary ion mass spectrometry (SIMS)

Junction space charge techniques have recently been reviewed in Refs. 30-32 and further information is given in Ref. 33. Basically, the idea is that

it is possible to change the occupancy of an impurity level in the band-gap as well as the amount of charge carriers created or annihilated via this level by external means such as light, temperature and electrical pulsing. If the impurity is situated in the depletion region of a pn-junction or a Schottky-barrier, the disturbance is monitored as capacitance- and current changes. All parameters of interest such as thermal and optical capture and emission rates are obtained either from only the magnitudes of the changes (steady-state techniques) or from both the magnitude and the time dependence (transient techniques).

In photocapacitance measurements, i.e. measurements of the change in capacitance induced by photons, it is possible to study, for instance, absorption from the ground state to the excited states. A great advantage of this technique is that the band to which the charge carrier is excited may easily be determined. There are, however, a number of drawbacks. A silicon diode does not work unless the temperature is relatively high ($T \geq 40$ K) which unavoidably broadens any structure due to excited states. The optical transitions take place in the presence of a strong electric field with a strong gradient. The transition probabilities to some excited states and even their energy positions may depend on the magnitude of electric field which gives an additional broadening.

If the absorption is measured in bulk material instead of a pn-junction, low temperatures may be used. The problem with the electric field also disappears. If the preparation of the sample is suitable and the mounting strain-free, the only remaining broadening is due to the neutral linewidth³⁴⁾. A drawback is that the sensitivity is less than for the junction technique.

For both manufacturers of, e.g., integrated circuits and for those active in semiconductor research, it is very important to know the chemical identity of a defect. For this purpose, SIMS or ESR combined with junction techniques have been used in this thesis. In a SIMS³⁵⁾ experiment, the sample surface is bombarded with primary ions and the secondary ions sputtering off the surface analyzed in a mass spectrometer. By peeling off successive layers of atoms, the sputtering beam eats its way toward the interior of the sample. In this way, the concentration profile of an impurity can be obtained. It is also possible to use junction techniques in determining concentrations profiles. If the profile measured with the

electrical method (junction technique) coincides with that obtained from the "atom-identifying" method (SIMS) the element related to the defect studied is revealed.

No information about the local defect structure is given from a SIMS experiment. This information is very important and can be obtained if the other identification method ESR^{36,37)} is used instead. Knowledge of the local defect structure is essential in understanding the electronic behavior of the defect. The interpretation of the ESR data was particularly simple in the case of chalcogens in silicon, since it turned out that they were spin-only centers with spin $S=1/2$. In such cases, the number of peaks of equal height in an ESR-spectrum is directly related to the nuclear spin of the isotope giving rise to the ESR-signal. The relative magnitudes of peaks with different heights corresponds to the natural abundances of the isotopes of a specific element. All isotopes with zero nuclear spin will show up as an unsplit, central line. Thus, in most cases, the element giving rise to the ESR signal may be unambiguously identified. By measuring the spectral dependence of the signal when shining light on to a sample, the spectral dependence of the photo-ionization cross sections of the defect can be obtained. If the spectrum coincides with that obtained from junction techniques, not only the element causing the defect but also the local defect structure are revealed, since interactions with neighbouring nuclei give rise to additional hyperfine structure of every ESR-line.

Summary

If sulfur, selenium or tellurium is introduced into silicon in the circumstances described in these papers two dominant donor levels appear. The deeper levels, the A-levels, are at energies 0.61, 0.59 and 0.41 eV respectively below the conduction band. In paper V, Ref. 38 and paper VI, it is shown using photo-ESR that the A-levels for selenium and tellurium are due to isolated chalcogen atoms occupying either substitutional or tetrahedral interstitial sites. From the spacing of the excited states seen in absorption and photocapacitance, it has been concluded that the A-levels for S, Se and Te are doubly-charged when empty. Unpublished photo-ESR results quoted in Ref. 39 together with results in papers I - VI support a simple model valid for all chalcogens. Emptying the A-level corresponds to removal of the second electron from an isolated chalcogen atom occupying a tetrahedral site, leaving a doubly-charged core behind. For simplicity, we assume the site to be substitutional.

The shallow levels, the B-levels, at 0.32, 0.31 and 0.20 respectively always have the same concentrations as the A-levels. The spacings of the excited states indicate that the B-levels are singly-ionized when empty. These facts support the model of an isolated substitutional chalcogen atom for which emptying the B-level corresponds to removal of the first electron. However, it should be kept in mind that so far no definite proof of this model has been given.

In paper III we used SIMS together with junction technique as an additional method for the chemical identification of the two selenium related levels A and B. It turned out that the concentration profile of selenium atoms was the same as those of levels A and B, which supports the model suggested above.

Unfortunately, it was not possible to measure the electron capture cross section of any A-level, since the capture was too fast. The B-levels are only singly-charged and are thus less attractive for electrons than the doubly-charged A-levels. The capture cross section of the B-levels of sulfur and selenium were measurable but the capture of tellurium was still too fast. The temperature dependence was $T^{-3.3}$ and $T^{-3.2}$ respectively in good agreement with Abakumov's theory²⁴⁾ if the recombination energy is carried away by a cascade of acoustical phonons.

In Table I thermal data on the centers studied in this thesis are presented and compared with optical binding energies. It must be remembered that any temperature dependence of ν , see Eqs. 8 and 9, would alter the energy values E_1 and E_2 and thus the assignments of the lowest cascade states. In paper IV the capture and emission processes are treated in a formally more correct way than in Ref. 25.

Absorption and photocapacitance measurements in papers V and VI and Ref. 38 show that all A- and B-centers have excited states that fit well in the energyspectrum scheme described above (see Fig. 3). Rydberg series as well as valley-orbit split $1s$ states are clearly visible in the spectra. In paper VI, it is shown that the $1s(T_2)$ state of the ionized chalcogen donor is split due to spin-orbit effects. The splitting is shown to be correlated to the atomic spin-orbit coupling of the impurity.

TABLE I. Capture (E_1) and emission (E_2) activation energies for chalcogen donors in silicon taken from papers I, II and V (see Eqs. 8,9 and figure 4). The following references are used for the binding energies (E_{opt}) of the ground states: S_A — Ref. 40, S_B — Ref. 41, Se — Ref. 42 and Te — Paper V. A tentative assignment of the lowest cascade state is given. The values in parentheses are the corresponding calculated binding energies and are taken from Faulkner (see Ref. 17), except $2s(A_1)$ which is taken from Altarelli (see Ref. 26). All energy values are in meV.

	E_{opt}	E_2	$E_{opt}-E_2$	E_1	lowest cascade state
S_A	613	587	26		$2p_{\pm}(26)$
S_B	318	302	16	17	$2s(A_1)(\text{unknown})$
Se_A	589	524	65		$2s(A_1)(73)$
Se_B	307	286	21	14	$2s(A_1)(\text{unknown})$
Te_A	411	364	47		$2p_0(46)$
Te_B	199	196	3		$3p_{\pm}(3)$

Results from other works

In papers I, II and V, surveys of earlier published results for different chalcogen centers are given. Although these papers were published quite recently, newer data have now appeared in the literature, which shows the great current interest in chalcogens in silicon. These new data will be commented on here. In general, the agreement with our results is very good.

Myers et al ⁴³⁾ reported an isotope shift for the sulfur deep level in silicon, which is in our notation the A -level. Using isothermal capacitance transients measurements, they found a shift of 14 meV between ^{34}S and ^{32}S . However, in a recent paper, Forman ⁴⁴⁾ investigated the absorption line that is generally referred to the $1s(A_1) \rightarrow 2p_{\pm}$ transition. He found an isotope shift of only 0.14 meV. Furthermore he claimed that the three strongest absorption lines all represent $1s(A_1) \rightarrow 2p_{\pm}$ transitions of different centers with slightly different binding energies of their $1s(A_1)$ states instead of the $1s(A_1) \rightarrow 2p_0$, $2s(T_2)$ and $2p_{\pm}$ transitions respectively of a single center. By assuming that "through a presently unknown mechanism" different mixtures of the slightly different centers

are present in ^{34}S and ^{32}S samples, he could account for the results of Myers et al ⁴³⁾, since only an average energy is measured in thermal measurements.

The proof of his assumption is the fact that the lines do not display the same annealing behaviour ^{44,45)}. An important fact is, however, that there are 10^{16} negatively charged boron atoms/cm³ in his samples. Thus, a strong electric field and perhaps even stress are present in the crystal. During annealing the situation may alter. The number of charged impurities may change and stress disappear. Forman's argument is not valid since different lines are not equally sensitive to the electric field as can easily be seen from a comparison of Figs. 10 and 12 in Ref. 34.

In a recent paper by Brotherton et al ⁴⁶⁾, the electrical properties of sulfur in silicon were studied using Hall effect and diode C-V type measurements. They interpreted their results in terms of two double donors, sulfur I (0.18 eV and 0.38 eV) and sulfur II (0.32 eV and 0.53 eV). The relative concentration of the two centers depends on the diffusion temperature. Sulfur I dominates at high temperatures and sulfur II at low. In addition, they found centers with energies < 0.1 eV which they assumed were sulfur-impurity complexes. For the sulfur II, 0.32 eV level, which would correspond to our B-level, they found the temperature dependence of the electron capture cross section to be $T^{-4.5}$.

In photoconductivity measurements, Humphreys et al ⁴¹⁾ found three neutral donors with binding energies 109.5, 187.2 and 318.4 meV respectively. The one at 318.4 meV is in excellent agreement with our B-level. However, our suggestion that the $2p_0$ state would have a binding energy of 17 meV is incorrect. From their data, it is clearly seen that the $2p_0$ state is at a distance of 11.4 meV from the conduction band, in good agreement with effective mass theory. The $2p_0$ and $2p_{\pm}$ states of an additional neutral center were also found giving a binding energy of 155 meV.

Sciar ⁴⁾ has investigated the effect of dopant diffusion vapour pressure on the properties of sulfur- and selenium-doped silicon IR detectors, keeping the diffusion temperature constant at 1200 °C. Both the activation energy obtained from the temperature dependence of the resistance

and the spectral photoresponse showed that the main impurity levels shifted to lower energies when the pressure increased. For S, the shift was $0.17 \rightarrow 0.10$ eV and for Se $0.30 \rightarrow 0.20$ eV. Sclar suggested that the formation of impurity molecules should increase with the diffusion pressure. Theoretical calculations have shown that impurity molecules have lower ionization energies than the corresponding isolated impurities⁴⁷⁻⁴⁹). Accordingly, he assumed that 0.17 and 0.30 eV were the ionization energies of neutral isolated impurities, whereas 0.10 and 0.20 eV were the energies of the corresponding impurity molecules. The assignment may be true for Se but is certainly not true for S, since Krag et al⁵⁰) have shown that the 0.17 eV level (or 0.19 eV which is a more proper value)⁵⁰) has trigonal symmetry and not the tetrahedral symmetry expected of an isolated substitutional impurity atom.

Swartz et al⁴²) have published optical excitation spectra of selenium doped silicon. They interpreted their results in terms of three double donors with binding energies 306.7 and 589.4 meV, 206.5 and 387.9 meV, 116.0 and 213.7 meV respectively. They ascribe the first double donor to an isolated substitutional Se-atom, the second to Se-pairs and the third to some selenium-related complex. The levels of the first double donor are in good agreement with the A- and B-levels in paper II and Ref. 38. As for the sulfur B-level, the binding energy of the $2p_0$ state is close to the effective mass value and is not equal to 14 meV as suggested in paper II.

Recently, electrical and optical properties of tellurium-doped silicon have been reported by Lin et al⁵¹). Using Hall effect, they found a thermal activation energy of 0.20 eV. From infrared absorption measurements, they obtained a binding energy of 198.8 meV for neutral Te donors in excellent agreement with the results for the B-level in paper V.

The data presented in this thesis and the results from the papers cited among the references suggest that the chalcogens may occupy different lattice locations (see Table II). The centers named A and B in this thesis are probably the ionized and neutral version of an isolated substitutional chalcogen impurity atom. Photo-ESR measurements³⁹) have shown that the ESR-signal from a sulfur pair could be quenched with light of energy larger than 0.37 eV. In the same samples, an ionized center with a binding energy of 0.37 eV was found using absorption techniques⁵⁰).

The sulfur center at 0.19 eV is neutral and has trigonal symmetry ³⁰⁾, which it would have if it originated from a pair. Since all excited states of the 0.37 and 0.19 eV centers of sulfur are identical to those of the 0.39 and 0.21 eV centers of selenium ⁴²⁾, it is tempting to use the same assignment in the selenium case. The corresponding centers for tellurium have not yet been found. Finally, a few other chalcogen-related centers have been observed but their origins are as yet unknown.

TABLE II. Ground state binding energies in eV of known chalcogen donors in silicon in eV. D refers to isolated substitutional chalcogen atoms, D_2 to chalcogen pairs and D_c to some chalcogen related defects.

	D^0	D^+	D_2^0	D_2^+	D_c	D_c^+
S	0.32	0.61	0.19	0.37	0.11 0.16	
Se	0.31	0.59	0.21	0.39	0.12	0.21
Te	0.20	0.41				

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Multivalley Splitting of $1s$ States for Sulfur, Selenium and Tellurium
Donors in Silicon.

by

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Abstract

Spin-valley splitting of the $1s(T_2)$ states of the ionized chalcogen donors S^+ , Se^+ and Te^+ in silicon is reported. The magnitude of the splitting is shown to be related to the impurity atomic spin-orbit splitting. The data are compared with the corresponding splittings of Sb^0 and Bi^0 donor impurities in silicon. Predictions of the magnitudes of the hitherto unobserved splittings of the neutral chalcogen donors and other group V donors are made. In addition, the binding energies of the $1s(T_2)$ states are compared with recent calculations by Altarelli. The available data on $1s$ states of group V and VI donor impurities in silicon are discussed.

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Introduction

The existence of six equivalent conduction band minima along the [100] directions in silicon has a profound influence on the energy states of donors ¹⁾. The central cell potentials of donor atoms occupying tetrahedral lattice sites, either substitutional or interstitial, will split a six-fold degenerated s-state into a singlet (A_1), a triplet (T_2) and a doublet (E) state, see Fig. 1. This splitting is usually referred to as valley-orbit splitting. Since the central cell potential is very localized, the splitting is much less for excited s-states than for the 1s state and negligible for p, d, ... states. These latter states are well described by effective mass theory (EMT) ²⁾.

Previous investigations have shown that the ground states of all group V and VI donors in silicon are 1s(A_1) states ³⁻⁵⁾, in agreement with the fact that the E and T_2 wavefunctions (unlike the A_1 wavefunction) have nodes at the impurity atom and are therefore less affected by the strong central cell potential.

If spin is included, the symmetry representations will be changed as follows: $A_1 \rightarrow \Gamma_6$, $E \rightarrow \Gamma_8$ and $T_2 \rightarrow \Gamma_7 + \Gamma_8$. The splitting of the T_2 level is due to its "valley induced" p-character which makes an interaction

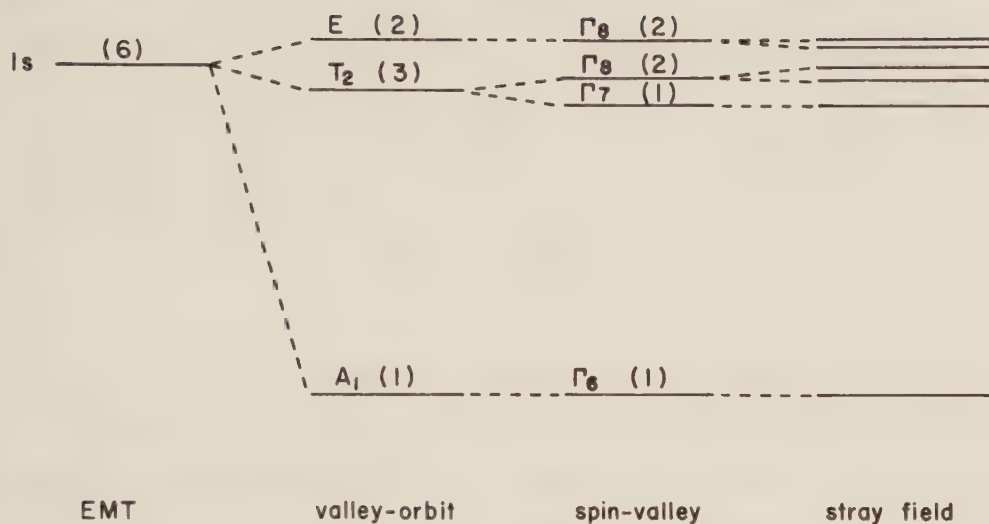


Fig. 1 Multivalley splitting of $1s$ donor states in silicon. The numbers in brackets are the degeneracies (excluding spin) of the states. For details, see text.

with the spin possible. This spin-"pseudo-orbit" splitting is sometimes referred to as spin-valley splitting.^{6,7)} (see Fig. 1). Due to their different degeneracies, the Γ_8 state will be shifted less than the Γ_7 state. If spin-valley interactions were absent, the unsplit $1s(T_2)$ state would lie at an energy of $E(T_2) = \frac{1}{3} E(\Gamma_7) + \frac{2}{3} E(\Gamma_8)$ ⁸⁾. Although the $1s(E)$ state cannot split, the $1s\Gamma_8(E)$ state may contain admixtures of T_2 states. However, to a first approximation, spin-valley interaction does not mix $1s\Gamma_8(E)$ states with $1s\Gamma_8(T_2)$ states, especially when the energy separation $1s(T_2) - 1s(E)$ is large⁹⁾.

In this paper we report on the energy-position of the $1s(A_1)$ and $1s(T_2)$ levels for some chalcogen donors in silicon. It has been shown earlier that after certain doping procedures, sulfur, selenium and tellurium may give rise to two dominant donors in silicon, the A and B centers^{3, 10-13)}. Although no definite proof has yet been given, the properties of these centers are best understood in terms of isolated substitutional donors. Filled A- and B-centers then correspond to singly-ionized (D^+) and neutral (D^0) impurity centers, respectively. The energy positions of the $1s(A_1)$ and $1s(T_2)$ levels are in this paper compared with both the effective mass theory²⁾ and recent calculations by Altarelli¹⁴⁾. Furthermore, the observed doublet in infrared absorption spectra for D^+ , earlier ascribed^{3,15)} to the transitions $1s(A_1) \rightarrow 1s(T_2)$ and $1s(A_1) \rightarrow 1s(E)$ respectively, is interpreted as arising from transitions from the ground state to the spin-valley split $1s(T_2)$ states. The magnitude of these splittings is compared with theory and with earlier experimental results on group V donors. Predictions for the magnitudes of the hitherto unobserved spin-valley splittings of the shallower chalcogen centers (D^0) are also made.

Experimental

The excited states of chalcogens in silicon have been investigated at low

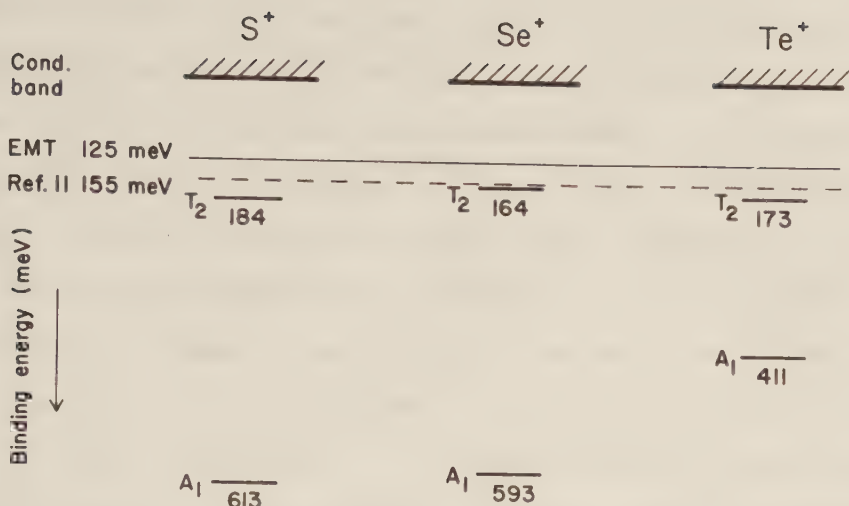


Fig. 2 Experimentally-determined multivalley split $1s$ states for the A-levels (D^+) in silicon doped with S, Se or Te. The thin solid line corresponds to the $1s$ level calculated from EMT (see Ref. 2). The dashed line indicates the position of the $1s(T_2)$ level as calculated by Altarelli (see Ref. 14). The numbers give the energy distance in meV from the conduction band. The values of the $1s(T_2)$ states are the mean values of the split states Γ_7 and Γ_8 :

$$E(T_2) = \frac{1}{3} E(\Gamma_7) + \frac{2}{3} E(\Gamma_8)$$

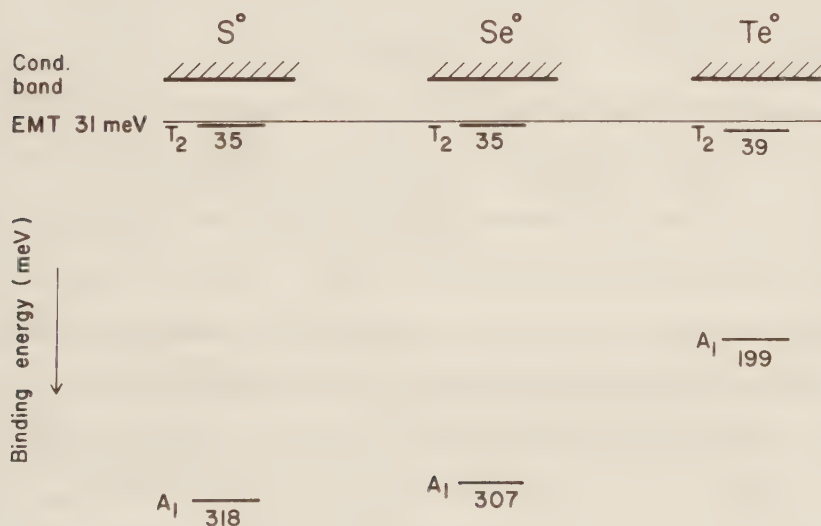


Fig. 3 Experimentally-determined multivalley split $1s$ states for the B-levels (D^0) in silicon doped with S, Se or Te. The same notations as in Fig. 2 is used.

temperatures (~ 6 K) using a Fourier spectrometer for infrared absorption. The preparation of the samples is described in Refs 3, 10 and 11. From the Rydberg series close to the conduction band edge, the binding energies of the $1s(A_1)$ ground states could be determined accurately by adding the EMT value of 6.40 meV ²⁾ to the energies of the transition $1s(A_1) \rightarrow 2p_{\pm}$ for the D^0 centers and $4 \times 6.40 \text{ meV}$ for the D^+ centers respectively (see Figs 2 and 3). The values obtained are in good agreement with earlier published data ^{3,13,15,16)} except in the case of Se^+ for which our binding energy is 4 meV larger than that in Ref. 15 although the excitation energy for the $1s(A_1) \rightarrow 1s(T_2)$ transition is the same. The S^0 data have been taken from Ref. 17 and are in good agreement with values given in Refs 11 and 13. The positions of the $1s(T_2)$ states deduced from absorption spectra are also shown in Figs 2 and 3. The $1s(T_2)$ states of the D^+ centers in Fig. 2 are all split, the splitting increasing with increasing mass of the impurity atom (see Fig. 4). The absorption doublet of S^+ has not been reported previously.

Discussion

From symmetry it can be seen that the transition $1s(A_1) \rightarrow 1s(T_2)$ is allowed whereas the transition $1s(A_1) \rightarrow 1s(E)$ is forbidden. In spite of this, both transitions are forbidden according to EMT since they are transitions between $1s$ states. For the transition $1s(A_1) \rightarrow 1s(T_2)$ to become an allowed transition, at least one of the states has to be mixed with other states, e.g., p -states or states from higher-lying conduction bands or the valence band. It is found experimentally that this mixing increases with increasing binding energy of the ground state. For shallow donors ¹⁸⁾ ($43 - 54 \text{ meV}$), no transitions among $1s$ states have been observed in silicon. For Bi ⁹⁾ (70 meV), a very weak doublet has been detected and for some of the chalcogens ^{3,13)} ($200 - 610 \text{ meV}$) the forbidden $1s$ transitions are obviously as allowed as the transitions from the $1s(A_1)$ state to the p -states.

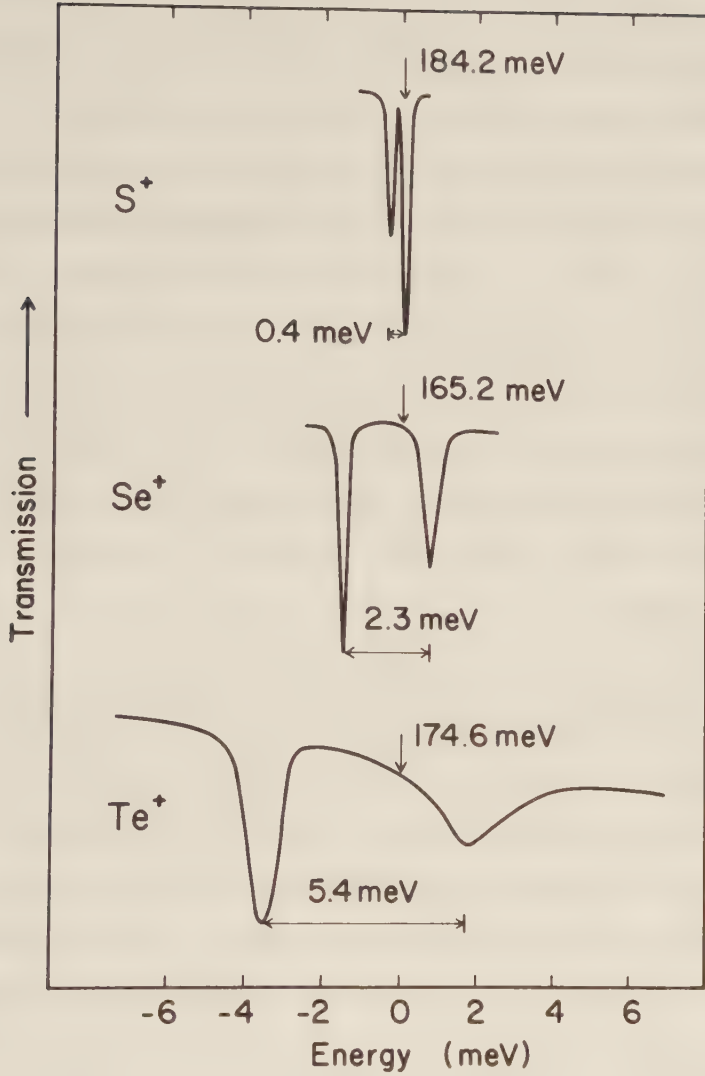


Fig. 4 Excitation spectra due to transitions from the ground states $1s(A_1)$ to the spin-valley split $1s(T_2)$ states for S^+ , Se^+ and Te^+ donors in silicon. The component to the right corresponds to $1s\Gamma_8(T_2)$ and that to the left $1s\Gamma_7(T_2)$. The origin of the energy scale is the transition energy to the unsplit $1s(T_2)$ state into which the two component of the doublet would reduce if the spin-valley interaction were absent.

For the transition $1s(A_1) \rightarrow 1s(E)$ to be allowed some random electric field or stress must exist in the crystal. However, it is unlikely that such disturbances would make the forbidden transition $1s(A_1) \rightarrow 1s(E)$ nearly as probable as the allowed transition $1s(A_1) \rightarrow 1s(T_2)$. In Refs 3 and 15, the doublets observed for Se^+ and Te^+ in silicon (Fig. 4) were interpreted as arising from the transitions $1s(A_1) \rightarrow 1s(T_2)$ and $1s(A_1) \rightarrow 1s(E)$. Since the absorption peaks in Fig. 4 are of the same magnitude, we have strong reasons to believe that the observed doublets are due to transitions from the ground states to the spin-valley split $1s(T_2)$ states, i.e., $1s\Gamma_7(T_2)$ and $1s\Gamma_8(T_2)$. Similar splittings have earlier been reported for Bi⁹⁾ and Sb¹⁸⁾ in silicon, although in the case of Sb the split $1s(T_2)$ states could only be observed as photo-excited transitions from thermally populated initial states to p-states.

It is not clear whether $1s\Gamma_7(T_2)$ or $1s\Gamma_8(T_2)$ should have the larger binding energy. The integrated absorption of the upper energy component in Fig. 4 is larger than the lower one suggesting that $1s\Gamma_8(T_2)$ with degeneracy 2 (excluding spin) has a smaller binding energy than $1s\Gamma_7(T_2)$ with degeneracy 1. If any random stress or electric field is present in the crystal, $1s\Gamma_8(T_2)$ will split (see Fig. 1) and the corresponding peak become broader. This effect is clearly seen in Fig. 4 for Se^+ and Te^+ . The upper component is considerably broader than the lower one, which indicates that $1s\Gamma_8(T_2)$ does lie above $1s\Gamma_7(T_2)$. The broadening, however, is large enough to imply some uncertainty in the magnitude of the splitting, since it cannot be taken for granted that the peak positions are not changed due to the presence of random stress or fields. By using uniaxial stress which splits the upper component into two peaks but leaves the lower component unsplit (see Fig. 1), Krag et al have shown that the ordering mentioned above is correct for Bi⁹⁾ in Si. Although the data for Sb¹⁸⁾ can be interpreted in the same way the splitting was not discussed in these

terms by the authors.

In Table I we have summarized all available data on $1s$ states for group V and VI impurities in silicon. It is readily seen that, although the ground state $1s(A_1)$ binding energies vary widely, the energy positions of the $1s(T_2)$ states are very similar and close to the EMT-value for all D^0 centers. Only for neutral tellurium is $1s(T_2)$ slightly deeper. The deviations are larger for the ionized (D^+) chalcogens. This is not surprising since the Bohr radii for D^+ states are only about 7 Å which should be compared with 20 Å for D^0 ones. Thus, the $1s(T_2)$ states for D^+ centers are more affected by the central cell potential than those for D^0 centers.

Altarelli¹⁴⁾ has recently carried out more detailed calculations of the binding energies of the excited states of an electron bound to a substitutional $+2e$ point charge in Si. The coulomb potential used was screened by a space dependent dielectric function $\epsilon(\vec{r})$. ($\epsilon(r) \rightarrow 11.4$ when $r \rightarrow \infty$ and $\epsilon(r) \rightarrow 1$ when $r \rightarrow 0$). Only the six lowest equivalent conduction band minima were included but both direct and umklapp intervalley interactions were taken into account. The binding energies obtained for the $1s(T_2)$ and $1s(E)$ states were 155 meV and 130 meV respectively (see Table I). It is interesting to compare these calculations with earlier calculations by Pantelides¹⁹⁾ from which binding energies of 127 meV [$1s(T_2)$] and 117 meV [$1s(E)$], were obtained when umklapp interactions were neglected. The deviation between the calculations may, however, partly be due to differing treatments of the intervalley kinetic energy²⁰⁾.

A valley-orbit splitting, $1s(T_2) - 1s(E)$, of about 25 meV is expected from Altarelli's calculations. This is much larger than the doublet splitting discussed above, in agreement with our assignment. Altarelli's calculated

TABLE I. Available data on the binding energies (in meV) of $1s$ donor states for Group V and VI impurities in silicon. Data labelled a are from absorption measurements at 10 K in Ref. 26, b are from electronic Raman scattering at about 20 K in Ref. 27, c and d are from absorption measurements at 30 K and 59 K respectively in Ref. 18, f are from absorption measurements at 10 K in Ref. 9 and g and k are from photoconductivity measurements in Refs 17 and 22 respectively. Data labelled p, q and r are calculated values from Refs 2, 14 and 21 respectively. All unlabelled data are from the present work.

	$1s(A_1)$	$1s(T_2)$	$1s\Gamma_7(T_2) - 1s\Gamma_8(T_2)$	$1s(E)$	$1s(T_2) - 1s(E)$
			exp.	calc.	
P^0	45.58 ^{a)}	33.90 ^{c)}		0.015	32.6 ^{b)} /32.57 ^{c)} 1.33 ^{c)}
As^0	53.77 ^{a)}	32.65 ^{d)}		0.09	31.5 ^{b)} /31.24 ^{d)} 1.41 ^{d)}
Sb^0	42.77 ^{a)}	32.88 ^{c)} 33.17 ^{c)}	0.29 ^{c)}	0.4	30.6 ^{b)} /30.58 ^{c)} 2.40 ^{c)}
Bi^0	71.00 ^{a)}	31.92 ^{f)} 32.92 ^{f)}	1.00 ^{f)}	1.1	
S^0	318.4 ^{g)}	35.1 ^{g)}		0.016	31.6 ^{g)} 3.5 ^{g)}
Se^0	306.7	34.5		0.11	
Te^0	198.8	39.1		0.6	31.5 ^{k)} 7.6
D^0	31.27 ^{p)} 47.5 r)	31.27 ^{p)} 31.4 r)			31.27 ^{p)} 30.6 r) 0.8 ^{r)}
S^+	613.5	183.9 184.3	0.4	0.3	
Se^+	593.3	163.7 166.0	2.3	1.7	
Te^+	410.8	171.0 176.4	5.4	6.3	
D^+	125.08 ^{p)}	125.08 ^{p)} 155 q)		125.08 ^{p)} 130 q)	25 ^{q)}

$1s(T_2)$ value is in fair agreement with our experimental data. If different impurity pseudo-potentials had been used, even the chemical shifts could perhaps have been reproduced. Furthermore, considering the depth of the energy level, it is not unreasonable to assume that wavefunctions originating from other bands should be taken into account. If these bands are conduction bands the binding energies would increase.

Altarelli et al ²¹⁾ have recently performed similar calculations on a substitutional +1e point charge in Si. Although due to insufficient screening of the extra proton these results cannot be directly related to those for neutral chalcogen donors, the data are nevertheless presented in Table I for comparison.

Recently, the $1s(E)$ states for S^0 ¹⁷⁾ and Te^0 ²²⁾ have been observed in photoconductivity measurements as dips in the photoconductivity above the ionization edge. The binding energies inferred were 31.6 meV for S^0 and 31.5 meV for Te^0 (Table I).

The energy positions of the $1s(E)$ states for Bi^0 , Se^0 and the ionized chalcogen donors have not as yet been reported. Since the corresponding absorption lines should be seen if the admixture of T_2 states due to spin-valley interactions is sufficiently strong, we have to conclude that this interaction is obviously not very strong. Using the data presented in Table I, one may anticipate that the $1s(E)$ states for Bi^0 and Se^0 probably lie 2 - 5 meV above the $1s(T_2)$ states whereas, in the case of ionized chalcogen donors the energy difference, according to Altarelli's calculations, should be at least 25 meV.

The experimentally-determined spin-valley splittings vary from 0.3 meV (Sb^0) to 5.4 meV (Te^+). The magnitude of this splitting should be approxi-

mately equal to the impurity atomic spin-orbit splitting reduced by the fraction of the donor envelope wave function in the central core region ⁶⁾. By using spin-orbit parameters and atomic radii from Ref. 23 together with Bohr radii deduced from experimentally-determined $1s(T_2)$ energy positions, the spin-valley splittings could be calculated. It turned out that the calculated values were 3 to 5 times smaller than those found experimentally. The best fit between the calculated and measured results was obtained by multiplying the calculated values by 3.7 (see Table I). Although the calculations are very crude they probably predict hitherto unobserved splittings within a factor of two. In this context it is interesting to note that unpublished calculations by L.M. Roth ²⁴⁾, suggest a splitting of 0.9 meV for Bi.

As for Sb^0 , the $1s(T_2)$ (and $1s(E)$) states of P^0 and As^0 were observed in photoexcitation measurements as transitions from thermally populated initial states to p states ¹⁸⁾. However, due to the larger binding energy of As, the measurement temperature was so high that the broadening of the linewidth made it impossible to observe the spin-valley splitting. For Se^0 and in particular Te^0 spin-valley splittings should be observable if suitable samples can be fabricated. For P^0 and S^0 , on the other hand, the spin-valley splittings will probably never be observed since the predicted splittings are comparable with the natural linewidth ²⁵⁾.

To summarize, we have shown that the $1s(T_2)$ states of S^+ , Se^+ and Te^+ exhibit spin-valley splitting related to the atomic spin-orbit splitting of the different impurities. The binding energies of the $1s(T_2)$ states are in reasonable agreement with recent calculations by Altarelli showing that the main part of the wavefunction of the electron in the bound $1s(T_2)$ state originates from the six lowest equivalent minima in the conduction

band. From the data presented in Table I, similar conclusions can be drawn for the $1s(T_2)$ and $1s(E)$ states of S^0 , Se^0 and Te^0 .

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